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14. ABSTRACT In the first three years of this grant we have made considerable progress towards the goals stated in the original proposal. To date we have made clean sources for propargyl radical, CH ₃ , F, Cl, Br and I. A total of 11 papers have been published during this grant period. We have a great deal of data that is currently being analyzed and will be published in the next grant period.					
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Final Report – June 2004: The Growth and Characterization of Metastable Free Radical Nanoclusters

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In the first three years of this grant we have made considerable progress towards the goals stated in the original proposal. At the time of writing the original proposal, we did not even have a source of radicals that was compatible with our helium nanodroplet apparatus. Nevertheless, the experiments we had carried out on simple gas phase species suggested that such experiment would be possible, if “clean” sources of radicals could be developed. The cleanliness of the radical sources is particularly important for helium nanodroplet experiments given that other species produced by the source would also be picked-up by the droplets. The resulting contamination would make it more difficult to observe the isolated radical species of interest.

Although we have developed a number of radical sources, including some based upon microwave and DC discharges, the most productive sources have so far been those based upon pyrolysis. The first such source consisted of a simple opened-ended quartz tube that was wrapped with a tungsten filament. Alumina tubes provided similar results. Our first application was to the study of the propargyl radical, produced by pyrolysis of propargyl bromide ¹. Other organic radicals have also been produced and will be the subject of future publications. The cleanest sources have been those for the halogen

atoms, formed by pyrolysis of the corresponding diatomic molecules. To date we have made clean sources for F, Cl, Br and I. We have obtained spectra for a wide range of molecules bound to these atomic systems. Of particular interest are the X-HF complexes. Although these heavy-light-heavy systems have been the subject of considerable experimental and theoretical studies, ours is the first to provide a detailed characterization of the bound states of these systems, including rotational and nuclear hyperfine structure. An example is shown in Figure 1, for the Br-HF complex.

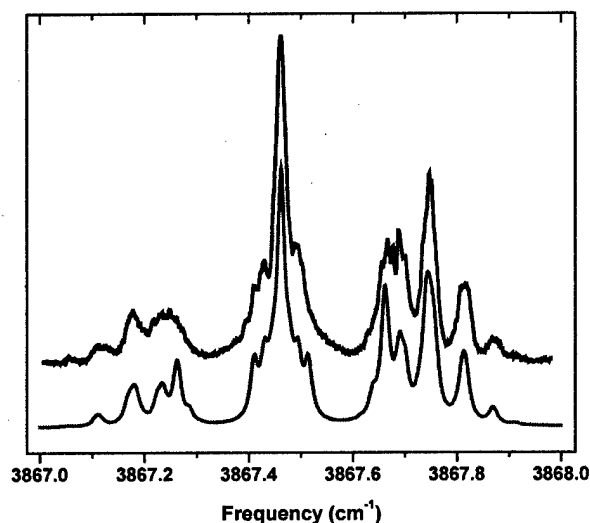


Figure 1: Rotationally resolved spectrum of Br-HF. The fine structure in the spectrum is due to nuclear magnetic hyperfine interactions.

Stark spectra have also been obtained for these species, in order to obtain the corresponding electric dipole moments. In fact, it is the analysis of this data that has held up the publication of this data, since we had to write a program for including Stark terms

in the Hamiltonian for these open shell species. This development work is now complete and the paper for Cl-HF, Br-HF and I-HF has been submitted for publication ².

We have used a combination of mass spectrometry and laser spectroscopy to study the recombination of halogen atoms in helium. Our first attempt at inhibiting recombination, by trapping the radicals in weakly bonded minima on a potential energy landscape, was based upon using a closed shell molecule as a "spacer" for keeping two halogen atoms apart. In particular, a linear cyanoacetylene (HCCCN) molecule was picked-up first by the helium, after which the conditions in the pyrolysis source were optimized for the pick-up of a single Br atom. We were able to spectroscopically identify two stable species, namely with the bromine atom bonded to either the hydrogen or nitrogen end of the molecule.

More interesting is the fact that at higher bromine pressures, optimal for the pick-up of two bromine atoms, a new peak appears in the spectrum, which we have assigned to the Br-HCCCN-Br complex. In part, this assignment is based on the fact that the frequency of this band is shifted from the monomer by an amount that is essentially the sum of the shifts for the Br-HCCCN and HCCCN-Br complexes. It is also interesting to note that while the Br-HCCCN is present in the spectrum regardless of the order of pick-up of the molecule and the Br atom, the band associated with the Br-HCCCN-Br complex is completely absent when the bromine is picked-up first. This makes sense, of course, since this isomer can only be formed if the molecule is there to help "steer" the atoms into the two remote positions. This is the first system we have observed in which two radicals are trapped in the helium in a non-reacted configuration.

We have developed a pump (PPLN-OPO)-probe (F-center) method that enables us to study the photoinduced isomerization of the complexes and molecules in helium^{3,4}. To date we have applied this to the study of closed shell systems. We find that vibrational excitation of one isomer gives the system sufficient energy to cause it to undergo isomerization. We are now in the process of applying this approach to the study of the Br-HCCCN-Br system, in the hopes that we can use the C-H stretch excitation to induce the reaction between the two bromine atoms. Indeed, the C-H stretch energy is more than sufficient to overcome the barriers between these two minima on the Br-HCCCN potential energy surface.

We are particularly interested in studying complexes of OH and CN radicals, since these are likely to have minima on the corresponding binary complex potential surfaces that represent pre-reactive complexes. The alumina and quartz tubes used in the above pyrolysis sources result in oxidation of these radicals. We have therefore developed a silicon carbide source that we feel will provide us with access to these systems.

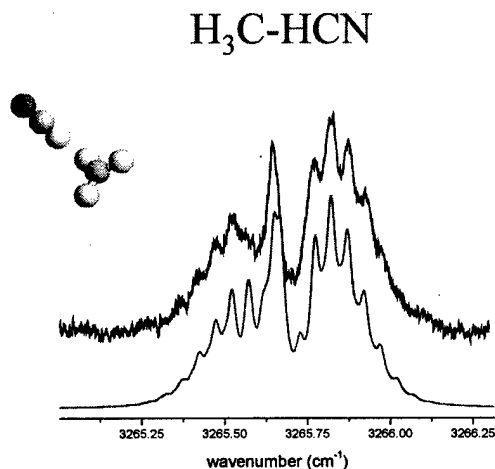


Figure 2: A rotationally resolved spectrum of the methyl-HCN complex.

We have also developed sources for CH_3 and NH_2 and complexes with these are currently being studied. For example, Figure 2 shows a spectrum of the $\text{CH}_3\text{-HCN}$ complex. Spectra have also been obtained for the $\text{CH}_3\text{-HF}$ complex, the post reactive complex in the prototypical F+CH_4 reaction, shown in Figure 3. Our work on the development of nitrogen atom and radical sources has progressed slowly, so we do not have any spectroscopic data on these systems. Nevertheless, work on these systems will also continue in the next grant period.

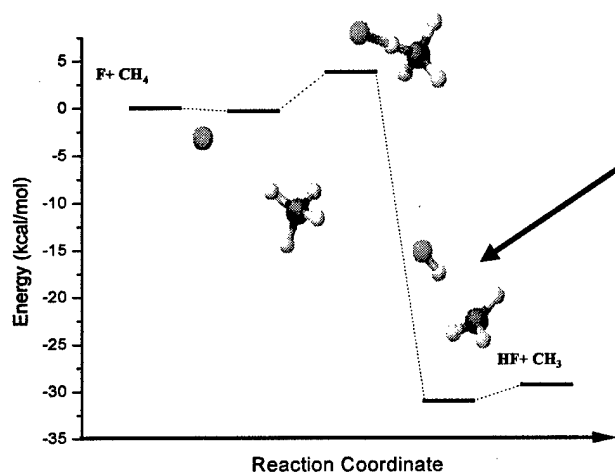


Figure 3: Reaction path for F-CH_4 .

As part of our interest in making the connection between the helium nanodroplet work and the studies that are being done in solid hydrogen, we also carried out extensive studies of HF and HCN in hydrogen clusters of varying size⁵⁻¹¹. These studies revealed a wide range of dynamical behavior, including internal rotation of the molecule within a cage of hydrogen molecules, which is now being studied by a number of theoretical groups.

References:

1. J. Küpper, J. M. Merritt, and R. E. Miller, "*Free Radicals in Superfluid Liquid Helium Nanodroplets: A Pyrolysis Source for the Production of Propargyl Radical*", J. Chem. Phys. **117**, pp. 647-652, [2002].
2. J. M. Merritt, J. Kupper, and R. E. Miller, "*High-Resolution Infrared Laser Spectroscopy of X-HF (X=Cl, Br, and I) Complexes formed in Helium Nanodroplets*", submitted, J. Chem. Phys. [2004].
3. J. M. Merritt, G. E. Douberly, and R. E. Miller, "*Infrared-infrared double resonance spectroscopy of cyanoacetylene in helium nanodroplets*", J. Chem. Phys. **121**, [2004].
4. G.E. Douberly, J.M. Merritt, and R.E. Miller, "*IR-IR Double Resonance Spectroscopy of Acetylene-HCN and Cyanoacetylene-HCN in Superfluid Helium Nanodroplets*" in preparation.
5. D. T. Moore, M. Ishiguro, and R. E. Miller, "*Binary complexes of HCN with H₂, HD and D₂ formed in liquid helium nanodroplets*", J. Chem. Phys. **115**, pp. 5144-5154, [2001].
6. D. T. Moore, M. Ishiguro, L. Oudejans, and R. E. Miller, "*High resolution infrared spectroscopy and ab initio calculations of the HCN-H₂/D₂ complexes*", J. Chem. Phys. **115**, pp. 5137-5143, [2001].
7. D. T. Moore and R. E. Miller, "*The Solvation of HF by Molecular Hydrogen: Helium Nanodroplet Vibrational Spectroscopy*", J. Phys. Chem. A **107**, pp. 10805-10812, [2003].
8. D. T. Moore and R. E. Miller, "*The Dynamics of Hydrogen-HF Complexes in Helium Nanodroplets*", J. Chem. Phys. **118**, pp. 9626-9636 [2003].
9. D. T. Moore and R. E. Miller, "*Rotationally Resolved Infrared Laser Spectroscopy of (H₂)_n-HF and (D₂)_n-HF (n=2-6) in Helium Nanodroplets*", accepted J. Phys. Chem. A, [2004].
10. D. T. Moore and R. E. Miller, "*Dynamics of hydrogen-HF complexes in helium nanodroplets*", J. Chem. Phys. **118**, pp. 9629-9636, [2003].
11. D. T. Moore and R. E. Miller, "*Size-dependent dynamics of a quantum solvent: Laser spectroscopy of HCN-(HD)_n grown in helium nanodroplets*", J. Chem. Phys. **119**, pp. 4713-4721, [2003].